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Isotopic evidence of magmatism and a sedimentary carbon source at the Endeavour hydrothermal system

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Abstract

Stable and radiocarbon isotope measurements made on CO_2 from high temperature hydrothermal vents on the Endeavour Segment of the Juan de Fuca Ridge indicate both magmatic and sedimentary sources of carbon to the hydrothermal system. The Endeavour segment is devoid of overlying sediments and has shown no observable signs of surficial magmatic activity during the ~20 years of ongoing studies. The appearance of isotopically heavy, radiocarbon dead CO_2 after a 1999 earthquake swarm requires that this earthquake event was magmatic in origin. Evidence for a sedimentary organic carbon source suggests the presence of buried sediments at the ridge axis. These findings, which represent the first temporally coherent set of radiocarbon measurements from hydrothermal vent fluids, demonstrate the utility of radiocarbon analysis in hydrothermal studies. The existence of a sediment source at Endeavour and the occurrence of magmatic episodes illustrate the extremely complex and evolving nature of the Endeavour hydrothermal system.

1. Introduction

Hydrothermal systems hosted on the Endeavour Segment of the Juan de Fuca Ridge are unique in their vigor[1], complex fluid chemistry[2], and seismically active geologic setting[3]. The Endeavour Segment is an intermediate spreading center, with a full spreading rate of 60 mm/yr. Since initial studies in 1980, it has been believed that the Endeavour Segment is in a tectonically controlled, extensional phase[1, 4] that has resulted in the formation of a 0.5 km wide, 100-200 m deep, steep-sided axial valley[1]. Axial parallel faults along the valley floor are believed to provide conduits for hydrothermal fluid flow, and many of the active hydrothermal vents at Endeavour are found along these features[1, 5, 6]. To date five vigorously venting hydrothermal vent fields have been discovered along a 15 km section of the spreading center, spaced at regular intervals of 2-3 km (Figure 1). The Endeavour has been characterized as a bare-rock fault controlled system devoid of significant sediment cover[1]. Anomalously high methane concentrations and depleted $\delta^{13}CH_4$ values in the vent fluids have led to the suggestion, however, that late Pleistocene sediments, which are ubiquitous 20 km north of the Endeavour, are a carbon source for the hydrothermal systems[7, 8]. Prior to 1999, revisitation of these fields over nearly 2 decades showed the hydrothermal fields to be stable with respect to vent fluid chemistry and temperature.

On 8 June 1999 the U.S. Navy's Sound Surveillance System (SOSUS) detected an earthquake swarm near the Endeavour Segment[9] which consisted of a moderate-size, 4.5 magnitude, initial shock followed by ~500 significant aftershocks during the subsequent two weeks[10]. This earthquake sequence was initially believed to be tectonic in nature after submersible observations in August-September 1999 failed to reveal evidence for new volcanic activity within the axial valley[9]. Recent analysis of vent fluid and volatile samples require a re-evaluation of this interpretation, suggesting that changes in fluid chemistry were the result of a magmatic event[11]. Isotopic evidence presented here corroborates this most recent hypothesis.

Carbon dioxide is the dominant volatile species in hydrothermal vent fluids from the Endeavour Segment. In submarine environments, CO_2 and H_2O are the dominant magmatic volatiles[12]. Carbon dioxide trapped as vesicles or dissolved in basalts at Endeavour exhibit a range of $\delta^{13}CO_2$ values (vs. VPDB) from –9.3 to –4.8‰[13]. Similar to other mid-ocean ridge systems, this variation has been attributed to fractionation during degassing of the magmatic CO_2 reservoir prior to eruption[14-17]. During exsolution of CO_2 from basaltic melts the vapor is enriched in ^{13}C by 2-4‰[16, 18], thus as degassing proceeds the remaining CO_2 dissolved in the melt becomes isotopically lighter. Based on isotopic studies, a primitive, relatively undegassed melt from a mantle source beneath the Endeavour has an enriched $^{13}CO_2$ signature of approximately –5‰[13], and would become increasingly depleted in ^{13}C as CO_2 is removed as vapor. Although no studies have been preformed, we hypothesize that magmatic degassing will not affect radiocarbon isotope values, as magmatic carbon is assumed to contain no ^{14}C.

2. Methods

All fluid samples were obtained between 1991 and 2000 using the submersible *Alvin*, and collected using a gas-tight titanium sampler[19]. The sampler is specifically designed to prevent fluid samples from degassing as ambient pressure is relieved upon ascent to the surface and subsequent processing. Upon shipboard arrival the sample is transferred from the gas-tight sampler into an evacuated gas-manifold vacuum line. The gas is stripped from the fluid through the addition of acid and successive agitation. The gas sample is then dried using a –60°C water trap, and measured manometrically. Multiple aliquots are flamed off into breakseals, which are archived and stored until on-shore analysis can be made. The fluid fraction of the sample is preserved for later analysis of major anions and cations.

The concentrations of archived gas samples were determined using gas chromatography techniques. Samples were prepared for isotopic analysis by cryogenically separating the fraction of CO_2 from the balance (CH_4, H_2, N_2, H_2S,). Freezing onto a finger of crushed Ag_3PO_4 separated CO_2 and H_2S, which have similar freezing points. All preparatory procedures were checked to ensure no isotopic fractionation occurred. Stable isotope measurements were made using a dual-inlet Finnigan 251 mass spectrometer. All values are reported in the conventional ‰ notation with reference to the Vienna Pee Dee Belemnite standard (VPDB). Radiocarbon measurements were made using conventional Accelerator Mass Spectrometry (AMS) techniques at the Center for Accelerator Mass Spectrometry at Lawrence Livermore National Laboratory. Radiocarbon isotope values are reported as fraction modern, which is the normalized specific activity ratio as defined by Stuiver and Polach[20].

Inevitably some seawater is entrained into the sample during collection, and thus measured $\delta^{13}C$ and fraction modern values must be corrected in order for the measurement to represent the pure vent fluid. As is standard in the analysis of hydrothermal vent chemistry, values were normalized to Mg. It is assumed that vent fluids have no Mg present, whereas seawater has [Mg] of 53 mmol/kg[2]. Using the measured Mg value of the sampled fluid, $[CO_2]$ (seawater) of 2.3 mmol/kg, $\delta^{13}CO_2$ (seawater) of –0.58‰, and fraction modern (seawater) of 0.76, a simple mass and isotope balance yields the corrected value. While this correction is generally small for the stable isotope value, it can be important for the radiocarbon value. All errors reported in Table S1 are the measurement and preparatory errors propagated throughout the necessary calculations in a Monte Carlo approach.

3. Results

This study shows that hydrothermal fluids sampled at all five vent fields along the Endeavour Segment yield $\delta^{13}CO_2$ values that range between – 9.85 and –6.07 ± 0.05‰ (see Figure 2a and Table 1). There is a clear division in the data: 1) a set of tightly grouped, relatively $^{13}CO_2$ enriched (-6.69 to –6.07‰) samples with elevated CO_2 concentrations[11] which were sampled from vents at the Main Endeavour Field (MEF) after the 1999 earthquake event; and 2) a set of isotopically lighter samples (-9.85 to –6.84‰) with lower CO_2 concentrations that were sampled between 1991 and 1998.

Samples taken within months of the 1999 earthquake show 3 to 5 times pre-1999 average CO_2 concentrations and have the most enriched $^{13}CO_2$ values reported from the Endeavour Segment. In 2000, the same vents sampled in 1999 exhibited relaxed CO_2 concentrations that were only slightly elevated compared to their pre-earthquake values, and corresponding $\delta^{13}CO_2$ values 0.44 ± 0.50‰ lighter. We interpret this temporary spike in isotopically heavy CO_2 as a pulse of fresh, undegassed magma emplaced beneath the Endeavour hydrothermal system. We further suggest that a sill or dike injection provided the initial burst of CO_2 as the melt rapidly degassed due to depressurization[21]. Additional CO_2, but in lower concentrations, would likely be released as the dike cooled subsequent to emplacement[22]. Non-eruptive diking events may contribute significant CO_2 to the carbon budget of the ridge. For example, using conservatively low estimates of dike dimensions and basalt degassing, a typical dike that intersects hydrothermal flow over a 1 m wide, 1000 m deep, and 5000 m long region[3, 23], and degasses 500 ppm of CO_2 in the cooling process[13, 24], would provide ~$1.7x10^8$ mol CO_2 to the hydrothermal system. This amount of CO_2 is of the same order of magnitude as the estimated yearly flux of CO_2 over the entire Endeavour segment[7, 25]. Thus, even a small ridge-parallel dike emplaced beneath the seafloor could supply sufficient CO_2 to account for the observed transient increase in CO_2 concentrations.

Additional evidence for a magmatic event as the cause for the 1999 earthquake sequence is seen in corresponding CO_2 radiocarbon data (Figure 2b). Vent fluid samples taken in 1999 have significantly lower CO_2 fraction modern values than samples taken in 2000 and prior to the earthquake event. Fraction modern[20] values for the three samples taken in 1999 from the vents Sully, Puffer and Hulk in the Main Endeavour Field are below 0.010, a value that approaches background levels for our radiocarbon measurements. It is expected that magmatic CO_2 will be "radiocarbon dead" (i.e. no measurable ^{14}C), as mantle carbon is derived from primordial degassing or recycled subducted material[26]. While samples taken directly after the 1999 earthquake clearly exhibit a magmatic ^{14}C signature, it is surprising that not all samples are radiocarbon dead, implying an additional source of CO_2 to the Endeavour hydrothermal system.

4. Discussion

The sample suite presented in this study show a linear relationship between $\delta^{13}CO_2$ and CO_2 fraction modern values, suggesting mixing of two CO_2 sources (Figure 3). The magmatic endmember of the mixing line was determined by extrapolating the data to a background fraction modern value, yielding a $\delta^{13}CO_2$ of –5.4‰. This $\delta^{13}CO_2$ value is in good agreement with previous measurements of CO_2 in Endeavour basalts thought to represent the least degassed lavas[13]. The younger, ^{13}C depleted endmember was placed on the best fit line through the data corresponding to reported ages of sediments found in the region. Heavy sedimentation occurred at the Cascadia Basin during the late Pleistocene, with a peak in accumulation rate between 27,000 and 15,000 years before present, and a maximum number of large, organic carbon rich turbidite flows occurring between 21,000 and 16,000 years before present[27, 28]. These sediment ages confine the $\delta^{13}C$ value of the young endmember to a range between –16 and –24‰. As the typically accepted value for marine sediments is –22‰[29], and the measured value of organic matter preserved in carbonate nodules from Middle Valley (a sedimented hydrothermal site 40 km North of Endeavour) is –18‰[28], this endmember implies an organic carbon source.

Based on these data we believe that the spread in the $^{13}CO_2$ and a $^{14}CO_2$ is due to mixing between a dead, ^{13}C enriched magmatic endmember, and a younger, ^{13}C depleted sedimentary endmember. Using our chosen endmembers, sedimentary CO_2 accounts for 3.5 ± 0.7 mmol/kg of the vent fluid CO_2, or roughly 20% of pre-earthquake CO_2 concentrations, and ~5% of the 1999 total CO_2. As there are no observable sediments on the Endeavour Segment we envision sediments buried beneath the spreading axis, through which hydrothermal fluids migrate in the upflow zone, as the additional source of CO_2. Considering ^{226}Ra-^{230}Th dating of Endeavour basalts yields an age of 5800-8100 years[30], the presence of sediments beneath the axis is chronologically feasible. This interpretation is consistent with anomalously high concentrations of NH_4^+, CH_4, B, Br, I, and trace alkalis in Endeavour vent fluids, which also indicate a sedimentary source[7, 8]. A buried sediment source of CO_2 suggests a finite supply of young, ^{13}C depleted carbon and, as this source is exhausted, a future shift towards the pure magmatic endmember is expected.

Stable isotope and radiocarbon isotope data presented here, strongly support the interpretation of Lilley et al.[11] for a magmatic pulse as the driving force for the 8 June 1999 earthquake sequence at the Endeavour Segment. Emplacement of a non-eruptive dike along axis is consistent with the transient increase in CO_2 concentrations, $^{13}CO_2$ enrichment, and $^{14}CO_2$ aging. While a degassing model could explain the 3‰ range in

$\delta^{13}CO_2$ values at Endeavour, it fails when considering the unexpected range in radiocarbon measurements. A mixing model involving magmatic and sedimentary endmembers is invoked to explain the linear relationship between $^{13}CO_2$ and $^{14}CO_2$. These findings suggest that the Endeavour Segment, and the hydrothermal system that it supports, may be evolving from a tectonically dominated phase to a more magmatically robust stage. Radiocarbon data clearly indicate a contribution of sedimentary carbon to hydrothermal systems hosted by the bare-rock Endeavour Segment. Based on these results a reevaluation of carbon reservoirs may be required at spreading systems along the global mid-ocean ridge network considering the potential for a non-magmatic carbon source. The radiocarbon data presented in this paper represent the initial effort to measure ^{14}C in hydrothermal vent fluids. As there is strong agreement between the radiocarbon results and other chemical data, it is our belief that ^{14}C-age dating is a valuable tool for hydrothermal vent fluid studies.

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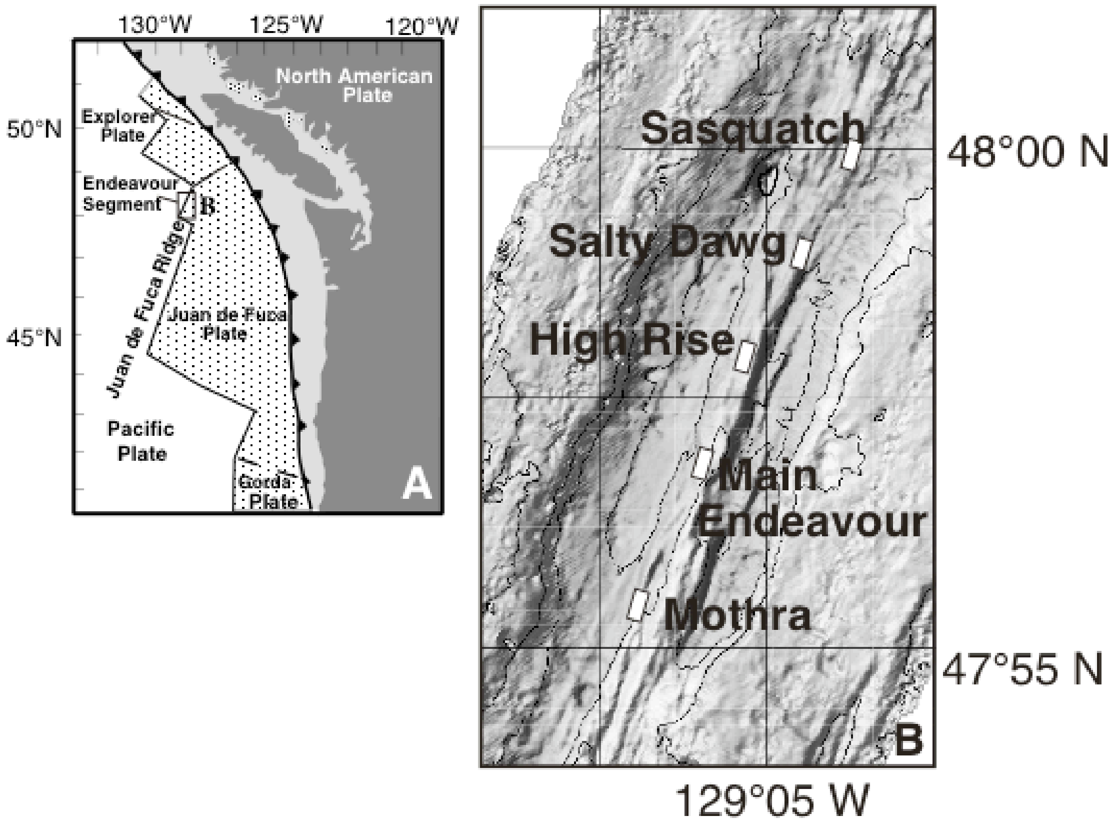
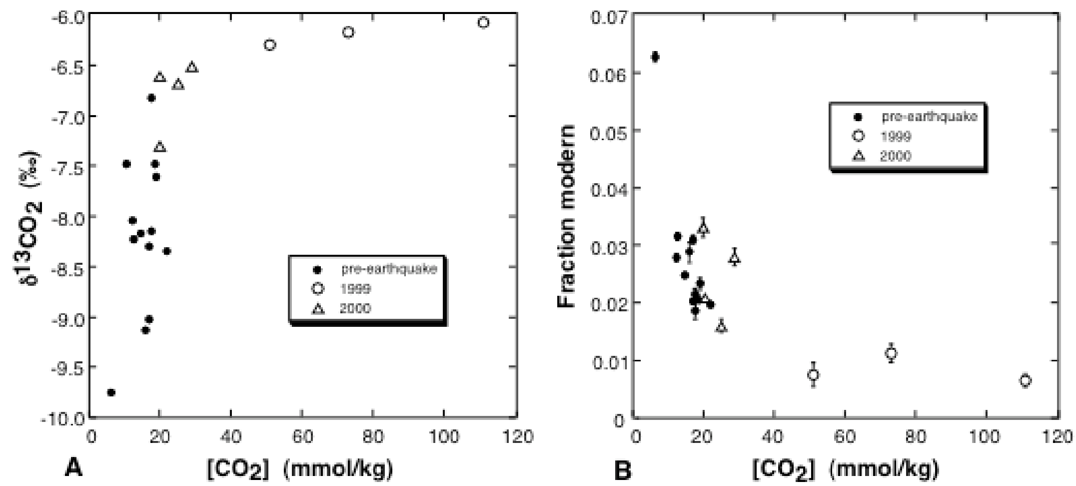
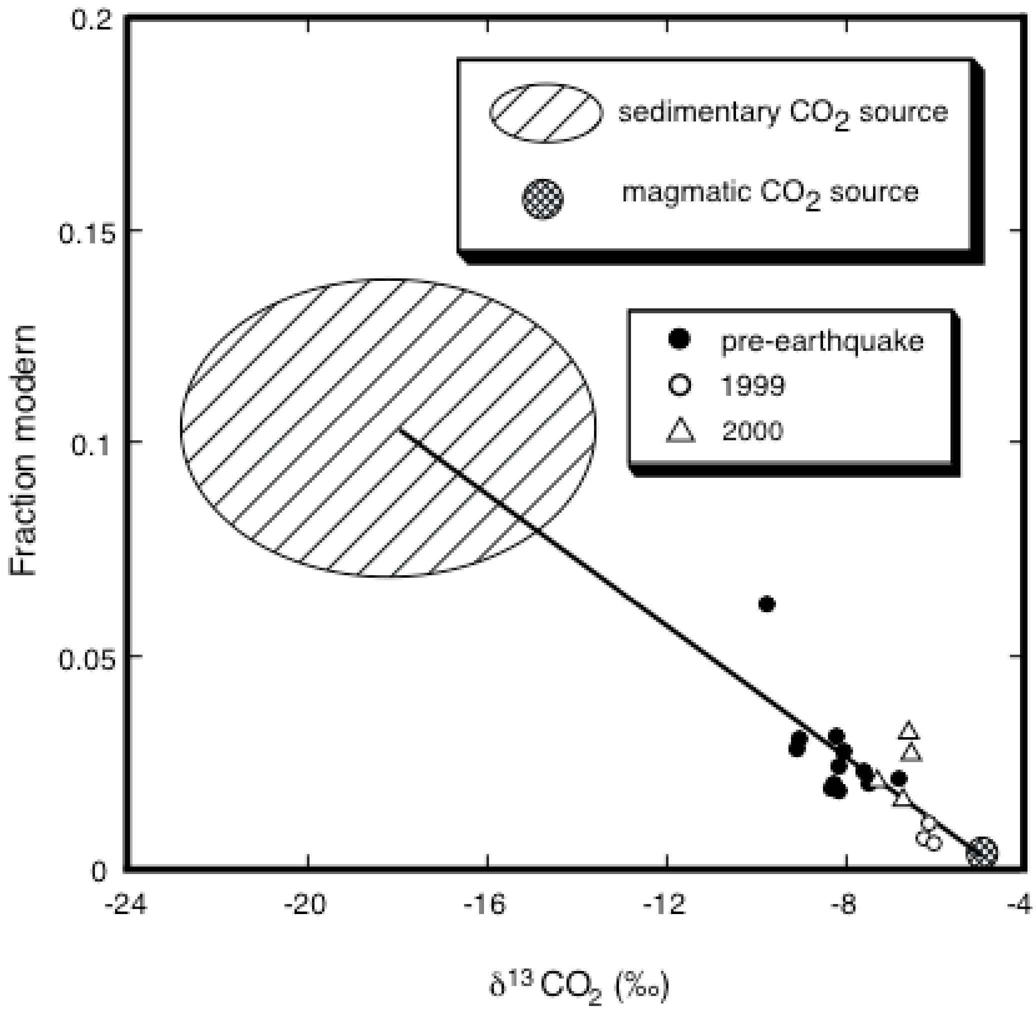

130°W
125°W
120°W
North American Plate
50°N
Explorer Plate
Endeavour Segment
B
Juan de Fuca Ridge
Juan de Fuca Plate
45°N
Pacific Plate
Gorda Plate
A
Sasquatch
48°00 N
Salty Dawg
High Rise
Main Endeavour
Mothra
47°55 N
B
129°05 W

Figure 1.



δ13CO2 (‰)
-6.0
-6.5
-7.0
-7.5
-8.0
-8.5
-9.0
-9.5
-10.0
0
20
40
60
80
100
120
A
[CO2] (mmol/kg)
pre-earthquake
1999
2000
Fraction modern
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
B

Figure 2.



0.2
0.15
0.1
0.05
0
-24
-20
-16
-12
-8
-4
Fraction modern
δ13 CO2 (‰)
sedimentary CO2 source
magmatic CO2 source
pre-earthquake
1999
2000

Figure 3.

Figure Captions

Figure 1, Geographical description of Endeavour Segment. (A) Location of Endeavour Segment on the Juan de Fuca Rdige, NE Pacific and (B) Distribution of the five known vent fields along the 020 trending axial valley.

Figure 2. CO_2 stable and radiocarbon isotope data plotted against concentration. (A) $\delta^{13}CO_2$ values plotted against $[CO_2]$ are shown as three separate groups. The pre-earthquake samples (filled circles) were taken between 1991 and 1998 and represent samples from the four known vent sites at the time (Sasquatch was discovered in 2000). The 1999 samples (open circles) were taken at the Main Endeavour vent Field (MEF) 2-3 months after the 8 June 1999 earthquake event. The 1999 samples show a large increase in $[CO_2]$ and a significant enrichment in ^{13}C, both indicative of an influx of primitive, magmatic CO_2. Samples from 2000 (triangles) were taken at MEF and at Sasquatch, and show a decrease in $[CO_2]$ and depletion in ^{13}C from 1999, suggesting that the magmatic CO_2 source was transient in nature. Error bars are not shown, as the 0.05‰ error associated with preparation and measurement of $^{13}CO_2$ is smaller than the marker size. (B) Fraction modern, as defined by Stuiver and Polach[20], is plotted against $[CO_2]$. This plot strengthens the conclusions from the $^{13}CO_2$ plot, as the 1999 values are nearly "radiocarbon dead", while the 2000 data appear similar to the pre-earthquake values, indicating a pulse of very old magmatic carbon. Error in radiocarbon measurements is shown for all data.

Figure 3. Mixing model plot for CO_2 at the Endeavour hydrothermal system. Magmatic and sedimentary endmembers are joined by a tie-line that indicates mixing between these two sources. Possible sources are indicated by the hatched regions; the sedimentary source is defined by the peak in sedimentation of the Juan de Fuca Plate, fraction modern 0.13 to 0.074 (16,000 to 21,000 years before present[27, 28]) and by $\delta^{13}C$ measurements made on carbonate nodules within these sediments (mean of –17.8‰, with a range of one standard deviation of ~7‰[28, 31]); the magmatic source is defined as a background (radiocarbon dead) fraction modern value, and a $\delta^{13}CO_2$ value of ~-5.0‰[13]. The tie-line represents the best fit of the data; and the endpoint in the sedimentary source is equal to the mean of the Middle Valley stable isotope data, as we feel this is the best constrained variable. Note that samples from 2000 may suggest an alternative fluid pathway after the earthquake.

Table 1.

Sample	Vent Name	Location	Year	Mg mmol/kg	CO_2 mmol/kg	Corrected $\delta^{13}CO_2$[a] ‰	Corrected $\delta^{13}CO_2$ ‰ error[b]	CAMS reference number	Measured fraction modern[c]	Measured fraction modern error	Corrected fraction modern[d]	Corrected fraction modern error[b]
2451-3,4	Hulk	MEF	1991	3.38	16.78	-9.03	0.05	78136	0.031	0.0007	0.03100	0.00078
2419-5,1	S&M	MEF	1991	1.6	14.30	-8.18	0.05	81560	0.02482	0.00063	0.02482	0.00066
2410-3,5	Bambi	High Rise	1991	0	17.49	-8.15	0.05	81563	0.01858	0.00152	0.01858	0.00148
3001-5,3	Dudley	MEF	1995	2.81	12.15	-8.05	0.05	81558	0.02791	0.00046	0.02791	0.00060
3002-2,3	Hulk	MEF	1995	2.51	12.37	-8.23	0.05	81559	0.03146	0.00054	0.03146	0.00063
3003-3,1	Bambi	High Rise	1995	0.75	17.29	-6.83	0.05	81569	0.02156	0.00101	0.02156	0.00100
2927-4,5	Boardwalk	High Rise	1995	1.32	21.71	-8.35	0.05	81564	0.01959	0.00063	0.01959	0.00063
3003-5,3	Godzilla	High Rise	1995	1.43	16.53	-8.30	0.05	81566	0.02025	0.00052	0.02025	0.00053
2929-6,5	Ventnor	High Rise	1995	1.16	15.57	-9.13	0.05	81562	0.02883	0.00170	0.02883	0.00171
3000-5,3	Salty Dawg	Salty Dawg	1995	1.71	18.80	-7.61	0.05	81561	0.02331	0.00108	0.02331	0.00109
3141-8,3	Mothra	Mothra	1997	1.55	6.14	-9.75	0.05	78134	0.0626	0.0007	0.06260	0.00082
3238-7,3	Puffer	MEF	1998	32.05	10.31	-7.49	0.09	81567	0.22395	0.00100	0.22395	0.00560
3236-7,7	Sully	MEF	1998	3.91	18.28	-7.49	0.05	81565	0.02064	0.00050	0.02064	0.00065
3468-11,3	Hulk	MEF	1999	2.06	50.76	-6.30	0.05	81573	0.00761	0.00207	0.00761	0.00204
3480-9,7	Puffer	MEF	1999	4.58	72.78	-6.17	0.05	81577	0.01125	0.00165	0.01125	0.00163
3474-11,3	Sully	MEF	1999	2.06	110.65	-6.06	0.05	81568	0.00662	0.00042	0.00662	0.00042
3612-12,3	Hulk	MEF	2000	0.65	24.58	-6.69	0.05	81825	0.01604	0.00043	0.01604	0.00043
3582-8,3	Puffer	MEF	2000	1.4	19.61	-6.62	0.05	81828	0.03306	0.00175	0.03306	0.00175
3570-10,3	Sully	MEF	2000	1.84	28.65	-6.53	0.05	81829	0.02797	0.00155	0.02797	0.00155
3622-9,3	Sasquatch	Sasquatch	2000	1.53	19.62	-7.31	0.05	78141	0.0206	0.0006	0.02060	0.00061

[a] $\delta^{13}CO_2$ values are corrected due to entrainment of seawater during the sampling process. We assume that vent fluids have a Mg of 0 mmol/kg, and seawater a [Mg] = 53 mmol/kg, [CO_2]=2.3mmol/kg, and $\delta^{13}CO2$ =-0.40‰, both measured values that agree with values from the literature.

[b] Reported errors associated with preparation and measurement were propagated through correction calculations using a Monte Carlo approach.

[c] Fraction modern is the normalized specific activity ratio as defined by Stuiver and Polach (1977).

[d] Measured fraction modern values are corrected using the same approach as for $\delta^{13}CO_2$. In this calculation a measured seawater fraction modern of 0.7588 (~2200 years, a reasonable value for NE Pacific Deep water) is used.